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ANTI-BIOFOULING PROPERTIES OF COMBLIKE BLOCK COPOLYMERS WITH AMPHIPHILIC SIDE CHAINS

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Novel polystyrene block copolymers with amphiphilic side chains were synthesized and evaluated for their anti-biofouling surface characteristics. The side chain consisted of a hydrophilic poly(ethylene glycol) (PEG) segment capped with a hydrophobic perfluoroalkyl segment. Surfaces prepared using these polymers showed a depth-dependent composition profile that was characterized using NEXAFS at the NSLS beamline U7A. The angle between the surface-normal and an in-plane electron detector was varied and partial electron yield NEXAFS spectra were acquired at each angle. An analytical framework to extract composition profile from the angle-dependent variations in Auger electron intensity was developed. The block copolymer surfaces, which showed surface segregation of the higher surface-energy PEG groups, were found to have promising fouling release properties when evaluated against the marine macroalga Ulva and the diatom Navicula.

Marine biofouling refers to the unwanted accumulation of marine organisms on an underwater surface. An environmentally benign strategy to tackle marine biofouling is the use of non-toxic polymer coatings that can resist bioaccumulation. Poly(dimethyl siloxane) (PDMS) elastomers are widely used as "fouling release" surfaces because they enable easy release of colonizing organisms.

Authors (from left) John Finlay, Ramakrishnan Ayothi, and lead researcher Sitaraman Krishnan

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While PDMS surfaces are quite efficient in the release of *Ulva*, they are ineffective against diatom fouling. The green macroalga *Ulva* and unicellular diatoms are the commonly found algae in marine biofilms. Their attachment to surfaces is achieved through secretion of adhesive glycoproteins, polysaccharides or proteoglycans. The attachment strength is determined by molecular interaction of these adhesives with the surface. Previous studies had shown that diatoms attached strongly to hydrophobic PDMS and weakly to hydrophilic glass surfaces, while *Ulva* exhibited an exactly opposite behavior. Our goal was to prepare biomaterial surfaces that minimized adhesion of extracellular adhesive matrices of a wide range of organisms.

Toward this goal, we attached PEGylated fluoroalkyl groups to a polystyrene-*block*-poly(acrylic acid) copolymer synthesized by ATRP. The amphiphilic polymers were expected to undergo an environment-dependent reconstruction as shown in **Figure 1**. Despite a slightly higher surface energy than polystyrene, we expected the PEG groups to segregate to the air-polymer interface because they were anchored to the low-energy perfluoroalkyl groups. Surface segregation of the PEGylated side chains was confirmed by NEXAFS. **Figure 2** shows the normalized partial electron yield NEXAFS spectra for four representative emission angles, ϕ. The sampling depth is proportional to $\cos\phi$. Hence, a higher emission angle implies that a thinner surface layer is being probed. The intensity of the C1s$\rightarrow\pi^*_{\Phi}$ resonance corresponding to the polystyrene block was found to be lower at a higher ϕ **(Figure 2)**. Conversely, the C1s$\rightarrow\sigma^*_{C-F}$ resonance intensity was higher at higher ϕ. Therefore, the polymer surface was enriched in the

PEGylated fluoroalkyl side chains relative to the polystyrene phenyl rings.

We have shown that the normalized intensity of the π^*_Φ resonance at a given emission angle, $I_\Phi(\phi)$, is proportional to the Laplace-transform of the concentration profile, $f_\Phi(z)$, of the phenyl-ring carbon atoms. Thus, $f_\Phi(z)$ could be determined from the experimental intensity versus emission angle data. Due to surface segregation of the amphiphilic block, only about 25% of the carbon atoms at the surface were from polystyrene, a concentration that was significantly lower than the value expected based on the block copolymer structure (~60%). The surface concentration of polystyrene decreased further upon water-immersion. The surface was immersed in water and the contact angle of an air bubble was measured over a period of 2 weeks. The captive-bubble contact angle decreased from 55° immediately after immersion to 31° after 2 weeks. The equilibrium contact angle was close to that of a pure PEG surface.

The amphiphilic surfaces showed a higher removal of both *Ulva* and *Navicula* compared to PDMS **(Figure 3)**. It remains to be determined whether these surfaces show similar fouling release properties against invertebrate larvae and other marine organisms.

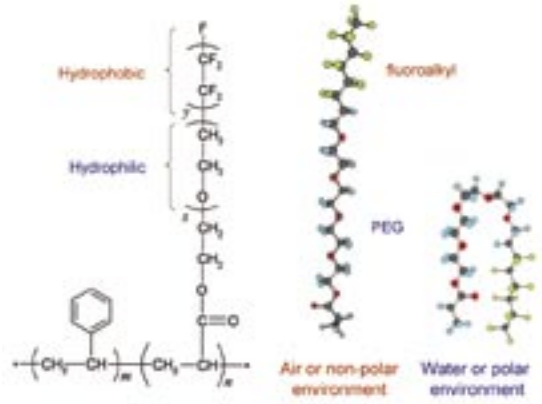

Figure 1. The left-hand side of this figure shows the chemical structure of the surface active block copolymer and its amphiphilic side group. In an air or non-polar environment, the fluoroalkyl group is exposed, but in water or polar environment, the polar PEG group occupies the surface.

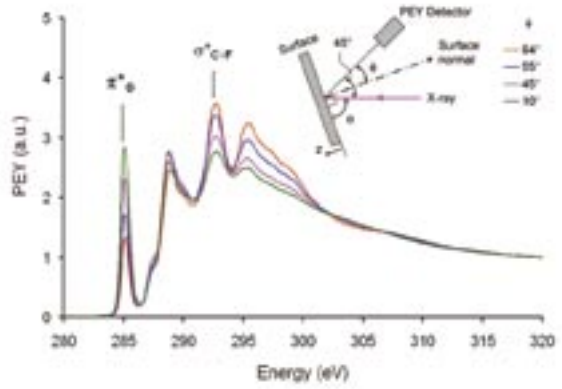

Figure 2. Normalized partial electron yield (PEY) NEXAFS spectra at different emission angles, ϕ, between the surface normal and the partial electron yield detector.

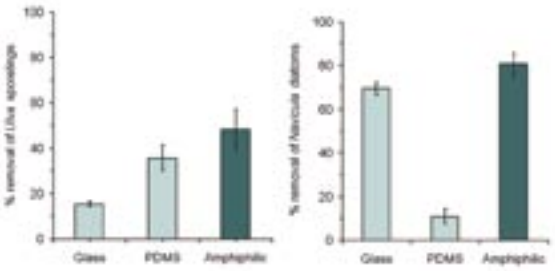

Figure 3. The left-hand side shows removal of Ulva sporelings (small, multicelled pregenitors to seaweed) and demonstrates that they are most easily removed from our new amphiphilic coating compared to PDMS (silicone rubber) or even glass. The right-hand side shows that Navicula diatoms are also very easily removed from the amphiphilic surface as well as glass whereas they adhere very strongly to silicone rubber.